ON AN EXPERIMENTAL MODIFICATION OF VAN DER WAALS'S EQUATION.

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§ 1. Introduction.

Some years ago[*] the author published a complete table of saturation constants derived from the well-known van der Waals equation—

$$\left(\pi+\frac{3}{\omega^2}\right)(3\omega-1)=8\vartheta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and, by their means, investigated the reliability of the equation in representing experimental results, especially within the saturation region. The equation was found, as expected, to give an excellent qualitative indication of the nature of the results to be expected under given conditions, while it completely failed to give any reliable quantitative estimates. Many modifications of the above equation have been proposed from theoretical considerations based upon assumptions more or less convincing, but the arbitrary nature of such assumptions seems to suggest that a direct appeal to experiment is to be preferred. In the following an attempt is made on the lines indicated by Kuenen[†] to modify the equation experimentally, and the improvement effected is brought to light by comparison with such data as are at present accessible.

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[*] J. P. Dalton: Phil. Mag. (6), 13, 1907, pp. 517–542.

[†] J. P. Kuenen: Die Zustandsgleichung (Vieweg), 1907, p. 128.

§ 2. THE VAN DER WAALS "a" AS A FUNCTION OF THE TEMPERATURE.

Following KUENEN, we shall, as a first approximation, regard the a of the equation—

$$\left(p+\frac{a}{v^2}\right)(v-b)=\mathrm{RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

as a function of T only, and b as a quantity which is independent of T. By applying well-known thermodynamical relationships we easily obtain—

$$a-\mathrm{T}\frac{da}{d\mathrm{T}}=v_{\mathrm{I}}v_2\left(\mathrm{T}\frac{dp_s}{d\mathrm{T}}-p_s\right) \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where p_s is the vapour-pressure at temperature T, and v_{I} and v_2 are the specific volumes of the respective phases of the complex on the same isothermal. Integration between any two temperatures gives—

$$\left(\frac{a}{\mathrm{T}}\right)_{\mathrm{I}}-\left(\frac{a}{\mathrm{T}}\right)_2=\int^{\mathrm{T}_2}\frac{v_{\mathrm{I}}v_2}{\mathrm{T}^2}\left(\mathrm{T}\frac{dp_s}{d\mathrm{T}}-p_s\right)d\mathrm{T} \quad . \quad . \quad . \quad (4)$$

As experimental substance Isopentane was selected, for which the saturation data have been determined with great accuracy by YOUNG,[*] From these data the integrand of (4) was evaluated in $\left[\frac{\mathrm{cm.}^6\ \mathrm{mm.\ Hg.}}{{}^\circ\ \mathrm{C.}}\right]$ units. These figures are given in column A of Table I. Integration was performed by means of a large-scale drawing on millimetre paper. The critical temperature was taken for the lower limit, and for the integration constant was written—

$$\left(\frac{a}{\mathrm{T}}\right)_k=\frac{3p_kv_k{}^2}{\mathrm{T}_k} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

For isopentane this becomes—

$$\frac{3\times 25015\times(4{\cdot}266)^2}{460{\cdot}8}=2964\left[\frac{\mathrm{cm.}^6\ \mathrm{mm.\ Hg.}}{{}^\circ\ \mathrm{C.}}\right]$$

Column B of Table I. gives the values obtained for the right-hand side of (4), and in the other columns are given values of a and of log a as functions of T.

The last column of the table and Fig. 1 show conclusively that log a is a linear function of T, so that we may write—

$$a=\epsilon^{\alpha-\beta\mathrm{T}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

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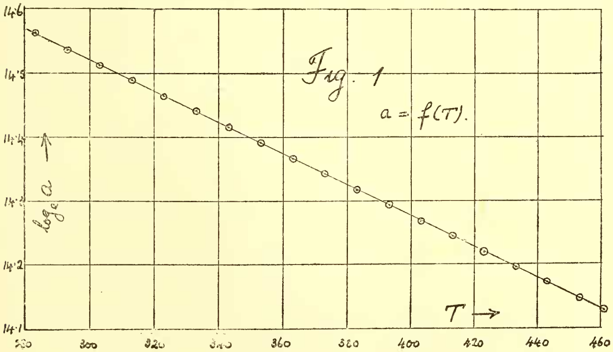
[*] S. YOUNG: Proc. Phys. Soc. 13 (1895), p. 602.

TABLE I.

$a = f(\mathrm{T})$: *Isopentane.*

T°.	A.	B.	$\frac{a}{\mathrm{T}}$	$a \times 10^{-6}$	$\log_{10} a$.	$\log_e a$.
283	48·37	4493	7457	2·1103	6·3244	14·5625
293	44·59	4066	7030	2·0598	6·3138	14·5381
303	41·07	3674	6638	2·0113	6·3035	14·5143
313	38·00	3310	6274	1·9637	6·2931	14·4904
323	35·30	2970	5934	1·9167	6·2826	14·4662
333	33·11	2653	5617	1·8705	6·2720	14·4418
343	30·76	2357	5321	1·8251	6·2613	14·4172
353	28·92	2079	5043	1·7802	6·2505	14·3923
363	26·87	1821	4785	1·7369	6·2398	14·3677
373	25·11	1578	4542	1·6942	6·2290	14·3428
383	23·62	1351	4315	1·6527	6·2182	14·3179
393	22·09	1137	4101	1·6117	6·2073	14·2928
403	20·74	937	3901	1·5721	6·1965	14·2680
413	19·44	749	3713	1·5335	6·1857	14·2431
423	18·26	573	3537	1·4962	6·1750	14·2185
433	17·06	409	3373	1·4605	6·1645	14·1943
443	15·76	257	3221	1·4269	6·1544	14·1710
449	14·97	—	—	—	—	—
453	14·39	106	3070	1·3907	6·1432	14·1452
456	13·83	—	—	—	—	—
458	13·40	—	—	—	—	—
459	13·18	—	—	—	—	—
460	12·89	—	—	—	—	—
460·4	12·60	—	—	—	—	—
460·8	12·38	0	2964	1·3658	6·1354	14·1273



The average value of β is 0·002446. This gives $a = 15{\cdot}255$ in the units employed.

With a view to the applicability of the law of corresponding states to the modified equation, (6) may be written in the form—

$$a = a_k \epsilon^{\beta T_k (1-\vartheta)} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where ϑ is the reduced temperature, and $\beta T_k = 1{\cdot}127$.

§ 3. THE MODIFIED EQUATION.

Equation (2) now takes the form—

$$\left(p + \frac{a_k \epsilon^{\beta T_k (1-\vartheta)}}{v^2}\right)(v-b) = RT \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If the law of corresponding states is to hold good, βT_k should be the same for all substances. Whether this is the case or not has not yet been determined, but it seems probable that it will not be found strictly constant, but to vary more or less with the complexity of the molecule, just as in the case of the reduced diameter slope.* In these circumstances we may, as a first approximation to a general equation, take βT_k to be unity, and equation (8) then yields on reduction—

$$\left(\pi + \frac{3}{\omega^2}\epsilon^{1-\vartheta}\right)(3\omega - 1) = 8\vartheta \,. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

In the sequel it is shown how much more closely this equation agrees with experiment than the original unmodified form.

§ 4. THE MODIFIED SATURATION CONSTANTS.

A direct calculation of these constants is best made by a substitution method. If we write—

$$\left.\begin{aligned} 3\omega_1 - 1 &= r\epsilon^{-\beta} \\ 3\omega_2 - 1 &= r\epsilon^{\beta} \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

and substitute in (9) and in the MAXWELL equation—

$$\int_{\omega_1}^{\omega_2} \pi d\omega = \pi_s(\omega_2 - \omega_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

we can eliminate π and ϑ and obtain—

$$2r = \frac{\epsilon^{2\beta} - \epsilon^{-2\beta} - 4\beta}{(\beta+1)\epsilon^{-\beta} + (\beta-1)\epsilon^{\beta}} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

$$= \frac{\sinh 2\beta - 2\beta}{\beta \cosh \beta - \sinh \beta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

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* Cf. E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN: Comm. Leiden, No. 131A (1913).

r is now evaluated from tables for various values of the parameter β, and the saturation constants then obtained. Even with tables the calculations are somewhat laborious, and it was found to be much easier to derive the modified constants from the table of unmodified constants referred to above. It is evident that the modification now introducted does not affect in any way the relative values of the saturation volumes;* hence if Π and Θ are the ordinary VAN DER WAALS saturation pressure and temperature for any pair of volumes, and π and ϑ represent the modified constants, we find—

$$\frac{1}{\Theta}=\frac{\varepsilon^{1-\vartheta}}{\vartheta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (14)$$

and—

$$\frac{\Pi}{\Theta}=\frac{\pi}{\vartheta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

If equation (14) is written in the form—

$$\log_e 10\Theta = \log_e 10\vartheta - 1 + \vartheta$$

it can be solved by inspection from a table of natural logarithms; π is then obtained from the known ratio $\frac{\Pi}{\Theta}$. Proceeding in this way, the following table of modified constants was obtained.

TABLE II.

Saturation Constants according to the Modified Equation.

ϑ.	π.	ω_1.	ω_2.	δ_1.	δ_2.
0·4964	0·0005275	0·3698	2506	2·704	0·0004
0·5493	0·002460	0·3777	592·6	2·646	0·0017
0·5980	0·007736	0·3864	203·6	2·587	0·0049
0·6430	0·01877	0·3960	89·15	2·525	0·01122
0·6850	0·03807	0·4068	45·98	2·459	0·02175
0·7245	0·06795	0·4188	26·61	2·388	0·03758
0·7615	0·1103	0·4326	16·73	2·312	0·05977
0·7966	0·1665	0·4485	11·18	2·230	0·08946
0·8298	0·2376	0·4672	7·811	2·140	0·1280
0·8614	0·3244	0·4896	5·643	2·042	0·1772
0·8916	0·4272	0·5174	4·173	1·933	0·2396
0·9204	0·5463	0·5534	3·128	1·807	0·3197
0·9480	0·6815	0·6034	2·349	1·657	0·4257
0·9745	0·8328	0·6841	1·727	1·462	0·5790
1·0000	1·0000	1·0000	1·000	1·000	1·000

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* If, as is in the meantime assumed, b is a constant.

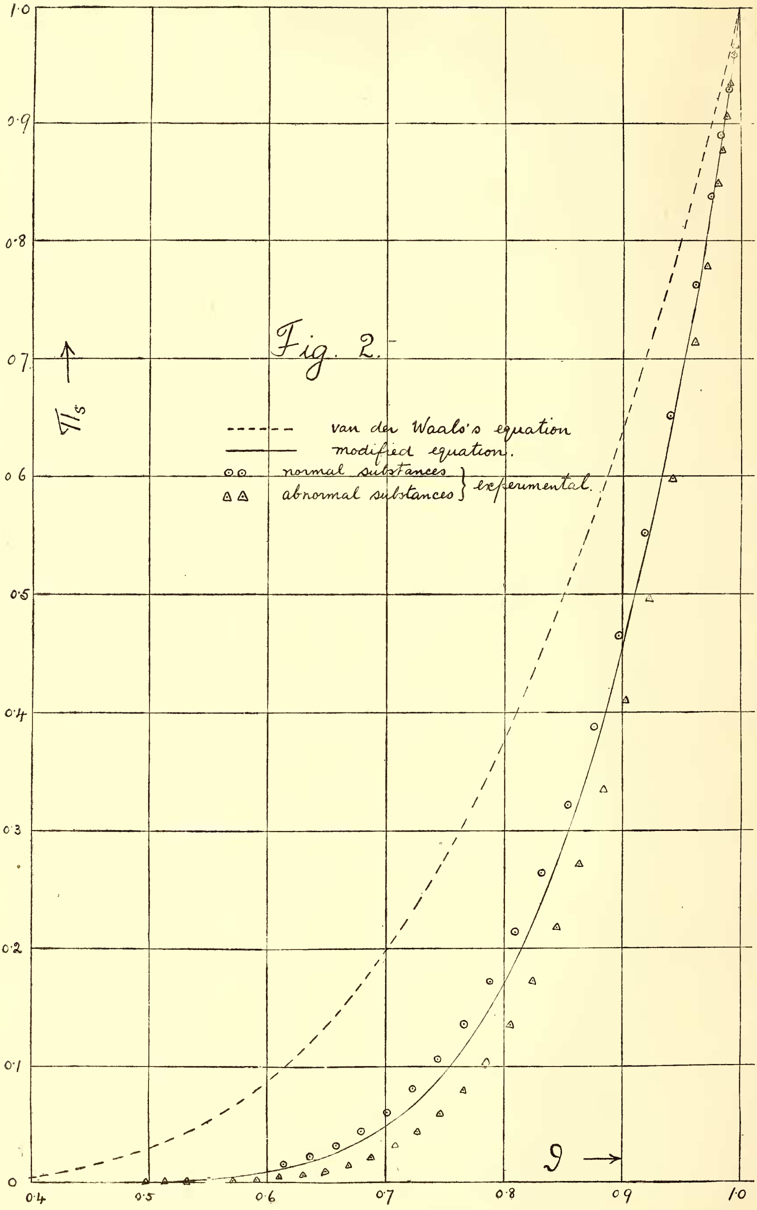

Fig. 2.

1·0
0·9
0·8
0·7
0·6
0·5
0·4
0·3
0·2
0·1
0
Π_s →
- - - - - - van der Waals's equation
———— modified equation.
⊙⊙ normal substances
△△ abnormal substances
} experimental.
ϑ →
0·4
0·5
0·6
0·7
0·8
0·9
1·0

The improvement effected by this modification is strikingly shown in Fig. 2. The reduced vapour-pressures from equations (1) and (9) are plotted, together with the experimental curves for isopentane* and methyl alcohol. If the law of corresponding states were rigorously obeyed the last two curves would be coincident; as long as such differences as these occur it is obviously impossible to represent the thermal behaviour of different substances by a single equation, and all that one can do is to construct an equation for a fictitious substance to serve as a type from which particular substances deviate more or less according to their molecular complexity. This is what Kamerlingh Onnes has done in deducing his "mean empirical reduced equation." Equation (9) seems, at least in so far as vapour-pressures are concerned, to be as good a type as can be found to represent both normal (isopentane) and abnormal (methyl alcohol) substances; it gives a much closer quantitative estimate than the unmodified equation, while, at the same time, it retains all the essential features of the original.

From the following table it will be seen that the modified equation is in good agreement with the van der Waals empirical vapour-pressure law—

$$\log \pi = f\left(1 - \frac{1}{\vartheta}\right) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (16)$$

as long as the temperature is not too low, and that the value of f at the critical point, 3·04, is not far from the corresponding values for such typically normal substances as carbon dioxide, 2·97, and isopentane, 2·95. The unmodified equation, on the other hand, as was previously shown,† gives values for f which deviate greatly from constancy, while the critical value is 1·72.

Table III.

ϑ.	f.	ϑ.	f.	ϑ.	f.
0·496	3·23	0·725	3·07	0·892	3·04
0·549	3·18	0·762	3·06	0·920	3·04
0·598	3·14	0·797	3·05	0·948	3·04
0·643	3·11	0·830	3·04	0·975	3·04
0·685	3·09	0·861	3·04	1·000	—

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* The carbon dioxide curve is coincident with this.

† *Loc. cit.*

§ 5. LATENT HEAT.

As a further test of the improvement effected by the foregoing modification, we may use the new constants for calculating values of the latent heat at different temperatures. The external work (reduced) of vaporization—

$$W/p_k v_k = \pi_s(\omega_2 - \omega_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

is only a fraction of the total latent heat, and yet even there an improvement is already evident, quite marked with respect to dependence on temperature although the change effected in the absolute magnitude of the work is not so great. VAN DER WAALS's equation gives 1·42 at $\vartheta = 0{\cdot}6$, rising to a maximum of 1·47 at $\vartheta = 0{\cdot}7$ and, of course, falling to zero at the critical point; while at $\vartheta = 0{\cdot}61$ isopentane gives 2·22, rising to a maximum of 2·42 at $\vartheta = 0{\cdot}76$. Values calculated from the saturation constants of Table II. give 1·57 at $\vartheta = 0{\cdot}60$ rising to a maximum, 1·80, at $\vartheta = 0{\cdot}76$. As before, carbon dioxide * and isopentane correspond very well.

The experimental values of the latent heat have been obtained from the well-known equation—

$$L = T \frac{dp_s}{dT}(v_2 - v_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

and the following table contains the values of the reduced latent heat, $L/p_k v_k$, thus found for isopentane.

TABLE IV.

$\frac{L}{p_k v_k}$: *Isopentane.*

ϑ.	$\frac{L}{p_k v_k}$	ϑ.	$\frac{L}{p_k v_k}$	ϑ.	$\frac{L}{p_k v_k}$
0·614	25·00	0·788	19·88	0·961	10·09
0·636	24·41	0·809	19·07	0·974	8·60
0·658	23·72	0·831	18·19	0·983	7·257
0·679	23·17	0·853	17·23	0·990	5·991
0·701	22·59	0·875	16·21	0·994	4·849
0·723	21·95	0·896	15·03	0·996	4·127
0·744	21·22	0·918	13·74	0·998	3·071
0·766	20·61	0·940	12·15	0·999	2·376

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* J. P. KUENEN and W. G. ROBSON: Phil. Mag. (6), 3, 155 (1902).

If van der Waals's equation is used for the calculation in conjunction with the thermodynamical relation—

$$L = T\int_{v_1}^{v_2} \frac{\partial p}{\partial T}\, dv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (19)$$

we find—

$$\frac{L}{p_k v_k} = \frac{8}{3}\theta \log_e \frac{3\omega_2 - 1}{3\omega_1 - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (20)$$

while the modified equation gives—

$$\frac{L}{p_k v_k} = \frac{8}{3}\vartheta \log_e \frac{3\omega_2 - 1}{3\omega_1 - 1} + 3\vartheta\varepsilon^{1-\vartheta}\left(\frac{1}{\omega_1} - \frac{1}{\omega_2}\right) \quad . \quad . \qquad (21)$$

When numerical values are obtained for (20), by means of the saturation constants of equation (1), we get, as the following table shows, reduced latent heats which are exactly one-third of the isopentane values at the same temperature. The same holds for carbon dioxide, for the latent heat curves for CO_2* and for isopentane practically coincide when reduced.

TABLE V.

$\frac{L}{p_k v_k}$: van der Waals.

ϑ.	$\frac{L}{p_k v_k}$	ϑ.	$\frac{L}{p_k v_k}$	ϑ.	$\frac{L}{p_k v_k}$
0·30	8·91	0·55	8·40	0·80	6·48
0·35	8·87	0·60	8·17	0·85	5·76
0 40	8·80	0·65	7·88	0·90	4·82
0·45	8·71	0·70	7·51	0·95	3·50
0·50	8·58	0·75	7·05	1·00	—

When the latent heat is calculated from (21) instead of (20), the greater part of this large discrepancy between actual and calculated values disappears. In the table, column A gives values of the first term of (21) and B gives values of the second term, each being obtained from the saturation constants of Table II.

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* Kuenen and Robson: *loc. cit.*

TABLE VI.

$\frac{L}{p_k v_k}$: *Modified Equation.*

ϑ.	A.	B.	$\frac{L}{p_k v_k}$
0·496	14·75	6·61	21·36
0·549	13·92	6·84	20·76
0·598	13·16	6·92	20·08
0·643	12·44	6·90	19·34
0·685	11·75	6·86	18·61
0·725	11·07	6·73	17·80
0·762	10·37	6·53	16·90
0·797	9·66	6·28	15·94
0·830	8·91	5·94	14·85
0·861	8·10	5·54	13·64
0·892	7·22	5·05	12·27
0·920	6·24	4·45	10·69
0·948	5·08	3·69	8·77
0·975	3·59	2·64	6·23
1·000	0·00	0·00	0·00

§ 6. ON THE SPECIFIC HEAT OF SATURATED VAPOURS.

In one of the papers to which reference has already been made (§ 1) the present writer used VAN DER WAALS's equation to investigate the behaviour of the specific heat of saturated vapours as a function of the limiting value of the ratio of their specific heats. As data were then (and still are) lacking by means of which the conclusions reached could be tested directly, an endeavour was made to obtain an experimental curve from the isopentane isothermals under a certain assumption regarding the behaviour of the specific heat at constant volume. That assumption has been criticized * as being not in accordance with the law of corresponding states, and it has, therefore, been abandoned in the following treatment of the problem. Specific heats are first obtained by means of the modified equation (which has been shown to approximate more closely to experiment than the VAN DER WAALS equation), and an experimental curve is then obtained from the isopentane isothermals, using the KAMERLINGH ONNES equation of state for determining the change of C_v with volume.

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* H. KAMERLINGH ONNES and W. H. KEESOM: Die Zustandsgleichung, *Encyc. Math. Wiss.*, v. 10, 937 (1912) or Comm. Leiden. Suppl. No. 23, p. 323.

If C_s represents the specific heat of the saturated vapour we may write

$$C_s = C_v + T\frac{\partial p}{\partial T_v}\frac{dv_s}{dT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

while C_v is connected with C_{v_∞} by the relation—

$$C_v = C_{v_\infty} + T\int_\infty^v \frac{\partial^2 p}{\partial T^2}dv \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

We may also write—

$$C_{v_\infty} = \frac{R_\infty}{\gamma_\infty - 1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

Combining these results we find for the specific heat of the saturated vapour in terms of reduced magnitudes—

$$C_s - \frac{R_\infty}{\gamma_\infty - 1} = \frac{p_k v_k}{T_k}\vartheta\left\{\int_0^\omega \frac{\partial^2 \pi}{\partial \vartheta^2}d\omega + \frac{\partial \pi}{\partial \vartheta_\omega}\frac{d\omega_s}{d\vartheta}\right\} \quad . \quad . \quad (25)$$

Along the inversion curve C_s vanishes; its equation is therefore given by—

$$\gamma_\infty = 1 - \frac{8}{3\vartheta\left\{\int_0^\omega \frac{\partial^2 \pi}{\partial \vartheta^2}d\omega + \frac{\partial \pi}{\partial \vartheta_\omega}\frac{d\omega_s}{d\vartheta}\right\}} \quad . \quad . \quad (26)$$

From equation (9) we find—

$$\frac{\partial \pi}{\partial \vartheta_\omega} = \frac{8}{3\omega - 1} + \frac{3}{\omega^2}\varepsilon^{1-\vartheta} \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

and—

$$\int_\infty^\omega \frac{\partial^2 \pi}{\partial \vartheta^2}d\omega = \frac{3}{\omega}\varepsilon^{1-\vartheta} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

so that the inversion curve becomes—

$$\gamma_\infty = 1 - \frac{1}{\frac{9\vartheta}{8\omega}\varepsilon^{1-\vartheta} + \vartheta\frac{d\omega_s}{d\vartheta}\left(\frac{3}{3\omega - 1} + \frac{9}{8\omega^2}\varepsilon^{1-\vartheta}\right)} \quad . \quad . \quad (29)$$

The right-hand member of the equation was evaluated from the constants of Table II., and the following results were thus obtained :—

TABLE VII.

Inversion Curve: Modified Equation.

ϑ.	γ_∞.	ϑ.	γ_∞.	ϑ.	γ_∞.
0·496	1·066	0·725	1·099	0·892	1·083
0·549	1·075	0·762	1·100	1·920	1·073
0·598	1·083	0·797	1·099	0·948	1·060
0·643	1·090	0·830	1·096	0·975	1·043
0·685	1·095	0·861	1·090	1·000	1·000

To obtain the experimental inversion curve, isopentane was again taken as a typical normal substance and equation (26) was applied to it in the unreduced form—

$$\gamma_\infty = 1 - \frac{R_\infty}{T\int_\infty^v \frac{\partial^2 p}{\partial T^2} dv + T\frac{\partial p}{\partial T_v}\frac{dv_s}{dT}} \quad . \quad . \quad . \quad . \quad (26')$$

The second term of the denominator has already been evaluated by DIETERICI[*] for isopentane, and his values have been used. The other term, which occurs only as a small correction, was evaluated by means of the KAMERLINGH ONNES mean reduced equation.[†] According to that equation the product, $\pi\omega$, is expressed as a finite series of inverse powers of the reduced volume—

$$\pi\frac{\omega}{k} = \vartheta\left(1 + B\frac{k}{\omega} + C\frac{k^2}{\omega^2} + D\frac{k^4}{\omega^4} + \ldots\right) \quad . \quad . \quad . \quad . \quad (30)$$

where B, C, D, etc., are expressed as polynomial functions of the temperature. The complete equation has five such "virial-coefficients," but for the present purpose the three given above were sufficient. k is the critical constant $\frac{RT_k}{p_k v_k}$.

We now find, to the degree of approximation required—

$$\frac{\partial^2 \pi}{\partial \vartheta^2} = \frac{k^2}{\omega^2}\frac{d^2}{d\vartheta^2}(B\vartheta) + \frac{k^3}{\omega^3}\frac{d^2}{d\vartheta^2}(C\vartheta) + \frac{k^5}{\omega^5}\frac{d^2}{d\vartheta^2}(D\vartheta) \quad . \quad . \quad (31)$$

and from this we easily obtain the correctional term—

$$T\int_\infty^v \frac{\partial^2 p}{\partial T^2} dv = -R\left[\frac{k}{\omega}\vartheta\frac{d^2}{d\vartheta^2}(B\vartheta) + \frac{k^2}{2\omega^2}\vartheta\frac{d^2}{d\vartheta^2}(C\vartheta) + \frac{k^4}{4\omega^4}\vartheta\frac{d^2}{d\vartheta^2}(D\vartheta)\right] \quad (32)$$

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[*] C. DIETERICI: Ann. d. Phys. 12, 602 (1903).

[†] KAMERLINGH ONNES and KEESOM: *op. cit.* p. 729.

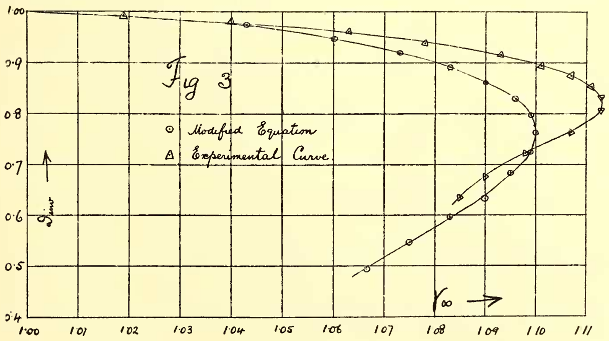
From the constants given by KAMERLINGH ONNES and KEESOM (*loc. cit.*) this expression was evaluated along the isopentane saturation line. As the DIETERICI values are a little irregular at the critical part of the curve, they were smoothed graphically before being used. In each case figures are given in cal/° C. and are for the gram-molecule.

TABLE VIII.

Experimental Inversion Curve.

ϑ.	$T\int_{\infty}^{v}\frac{\partial^2 p}{\partial T^2}dv$.	$T\frac{\partial p}{\partial T_v}\frac{dv_s}{dT}$ (smoothed).	γ_{∞}.
0·636	0·5	−24·0	1·085
0·679	0·7	−22·7	1·090
0·723	1·0	−21·3	1·098
0·766	1·3	−19·8	1·107
0·809	1·6	−19·1	1·113
0·831	1·8	−19·4	1·113
0·853	1·9	−19·8	1·111
0·875	2·1	−20·6	1·107
0·896	2·3	−21·9	1·101
0·918	2·6	−24·0	1·093
0·940	2·9	−28·2	1·078
0·961	3·3	−34·8	1·063
0·983	3·8	−53·8	1·040
0·994	4·4	−114·4	1·018
1·000	—	—	—

Fig 3



Both curves (Fig. 3) exhibit the same general features as those previously obtained—for γ_∞ greater than a certain critical value, C_s is negative for all values of ϑ; for smaller values of γ_∞, we have C_s becoming negative, zero, positive, zero, and again negative as ϑ increases towards unity; the two inversion temperatures are further apart the lower the value of γ_∞, and they coalesce at the critical γ_∞. But this critical value is somewhat smaller than expected, and, if the values previously quoted for γ_∞ are correct, would seem to exclude the possibility of inversion occurring with Acetone, Benzene, and Chloroform, for which it has actually been observed. But it is quite possible that the values of γ which were then used were obtained under conditions not sufficiently far removed from the state of saturation to allow of their being regarded as identical with the state of a perfect gas. The WIEDEMANN γ for Benzene, for instance, was 1·129, while a more recent determination by STEVENS* gives (at ± 100° C.) 1·105; according to the present curves the former value would render C_s always negative, while the latter would give inversion at $\vartheta = 0{\cdot}75$ and $\vartheta = 0{\cdot}88$. For isopentane, for which γ_∞ is probably 1·08, the experimental curve would give inversion at $\vartheta = 0{\cdot}61$ and $\vartheta = 0{\cdot}74$, values which are, as one would expect, almost identical with those deduced by DIETERICI from his own experiments in conjunction with YOUNG's isothermals. But the paucity of experimental data for both γ_∞ and C_s renders it impossible to test the quantitative value of the foregoing conclusions.

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* E. H. STEVENS: Ann. d. Phys. (4), 7, 285, 1902.